Preventing and inhibiting

Stopping this electrochemical phenomenon isn’t entirely possible,

KEY CONCEPTS

• For most metals, it’s not possible to completely prevent all corrosion, nor is it possible to undo corrosion once it takes place.

• There needs to be more emphasis across all industries on corrosion inhibition and prevention than corrosion repair.

• Two research drivers are environmental regulatory legislation and the trend toward machining lighter metals like aluminum and magnesium.
At 5 p.m. on Dec. 15, 1967, the Silver Bridge in Kanauga, Ohio, suddenly crumbled into the Ohio River. Bystanders said the collapse was so quick and dramatic that it sounded like a shotgun blast. They watched as the collapsing sections of the bridge folded into each other like a deck of cards.

Horrified witnesses saw vehicles floating downstream while passengers frantically and futilely beat on their windows trying to escape. A truck driver stood on top of his cab, screaming for help as his truck slowly floated downstream and disappeared into the water.

Of the 37 vehicles that were crossing the bridge, 31 plummeted into the icy water below. Many bystanders tried to pull struggling motorists out of the water. Rescue crews, on the scene in minutes, were able to save some, but in all 46 souls were lost.

A comparatively minor, yet significant, consequence was that a critical transportation connection between West Virginia and Ohio was suddenly gone.
The 2,235-foot long, two-lane suspension bridge was designed under the exacting specifications of the American Society of Civil Engineers and completed in 1928. The Silver Bridge—so named because it was the U.S.’s first aluminum-painted bridge—had eyebars that were linked in chain-like pairs. An enormous pin passed through the eye and linked each piece to the next.

The cause of failure was attributed to a minute cleavage fracture in a single eyebar that occurred when the eyebar was originally cast. Over the years, stress corrosion and corrosion fatigue allowed the crack to grow, causing the entire structure to suddenly fail. The two contributing factors over the years continued to weaken the eyebar and, unfortunately, the entire structure.

Another factor that led to the collapse was the ever-increasing weight of new cars and trucks. When the bridge was originally designed, the Model-T Ford weighed 1,500 pounds. In the year the bridge collapsed, the average new car weighed more than 4,000 pounds. In 1928 state law prohibited the operation of any vehicle whose total weight was more than 20,000 pounds. The year of the collapse, that limit was 60,800-70,000 pounds (depending on permits).

After the collapse, President Lyndon Johnson initiated a national probe to determine the safety of the nation’s bridges—especially the 1,800 bridges that were at least 40 years old.¹

Unfortunately, the Silver Bridge disaster is only one of many bridge failures due to corrosion. It was the cause of the 1983 Mianus River Bridge collapse in Connecticut and the 2003 Kinzua Bridge collapse in Pennsylvania.

Why are bridges so vulnerable? Partly because the primary metal used in bridges is iron, and iron is extremely susceptible to corrosion degradation and a resulting process colloquially known as “rust smacking”—rust expands whatever it feeds off of, appearing to bubble up the material. When enough rust accumulates, the expansion creates an impressive force that actually pries apart adjacent structural components. Also, in reinforced concrete bridges, the corrosion of concrete-encased steel and iron can cause the concrete to spall, creating severe structural problems.

The issues of corrosion and corrosion prevention extend way beyond bridges; they’re apparent everywhere, from junkyards to airplane hangars.

OVERVIEW

The terms rust and corrosion are not interchangeable. Corrosion is the broad term for the process of a chemical reaction that breaks down and eats away a variety of materials. Rust is a specific type of corrosion that consists of iron reacting with water or humidity and forming iron oxide. It can only be made with water, oxygen and iron (iron is relatively unaffected by pure water or by dry oxygen). Rust and iron oxide are one and the same.

Rust denotes a series of iron oxides. Commonly it refers to red oxides, formed by the reaction of iron and oxygen in the presence of water or air moisture. But there are other forms of rust, such as that caused by the reaction of iron and chlorine in an oxygen-less environ-

Corrosion is the broad term for the process of a chemical reaction that breaks down and eats away a variety of materials.

Conn. “It can, however, postpone rust for a length of time. This can be for a short time during storage before a subsequent step such as painting, or it can be designed to prevent rust for the useful life of the part or machine.”

**INDUSTRIES MOST AFFECTED**

Corrosion hurts some industries more than others. Not surprisingly, some of the industries most affected are the ones that are leading research efforts into corrosion prevention and control. But there are other industries, profoundly affected by corrosion, that have resigned themselves to continuous replacement of rusted parts and equipment.

**Motor vehicles.** Before the mid-1970s, old corroded car...
The automotive industry is a poster child for how well proper design, material selection and treatment can control and prevent corrosion.

bodies used to be a mainstay in most areas, but not anymore. The automotive industry is a poster child for how well proper design, material selection and treatment can control and prevent corrosion. When auto and equipment makers began to use galvanized steel and incorporate corrosion-limiting design and manufacturing techniques, steel components became corrosion-proof or at least corrosion-resistant.

Because dramatic corrosion reduction boosts resale values, the consumer is the big winner. But the environment benefits as well. Now even older cars that are no longer operational can be completely recycled into scrap metal.

Aircraft. While aircraft are subjected to the same corrosion problems as automobiles, the aircraft industry lags behind in terms of corrosion control. For aircraft, corrosion is a major useful life factor and a potential safety factor. Corrosion has become a very costly factor in U.S. military aircraft.

Oil and gas industry. Corrosion continues to be a problem in all facets of the oil and gas industry. Studies show direct corrosion costs in related industries as follows:2

- Gas and liquid transmission pipelines: $7 billion a year
- Hazardous materials storage: $7 billion a year
- Gas distribution: $5 billion a year
- Petroleum refining: $3.7 billion a year
- Oil and gas exploration and production: $1.4 billion a year
- Hazardous materials transport: $0.9 billion a year.

Because of tighter governmental scrutiny and regulation, the oil and gas industry has implemented costly measures to reduce its impact on the environment. These measures extend to the types of products they produce and the way they operate.

Water and sewage. Surprisingly, very little is being done to prevent corrosion in the water and sewage industry, one of the industries most affected by corrosion. The usual strategy is repair rather than prevention. Despite a number of attempts, there is still no good way to assess the condition of the lines before a breakage occurs.

INHIBITORS VS. PREVENTIVES
Experts don’t agree on the difference between corrosion inhibitors and corrosion preventives and when each is best applied.

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Figure 2 | Bill Kingston of King Industries, Inc., standing in front of a Kesternich Cabinet Cyclic Humidity Chamber (during the 16-hour dry phase of the cycle). [Courtesy of King Industries, Inc.]

“I have always believed that a corrosion inhibitor is added to a synthetic, semisynthetic or soluble base MWF fluid to protect the freshly worked piece and the tool doing the work from corrosion during the MWF process,” says Fred Cuneo, former Lubrizol manager and current renewable resource rust preventive consultant for Custom Chemical Corp. in Roebuck, South Carolina. “On the other hand, a corrosion preventive, usually diluted with solvent, oil or as a water emulsion, is used to protect the freshly worked and cleaned piece prior to storage or transportation.”

Cuneo adds that corrosion inhibitors should always be added to MWFs whenever the metal surface is exposed to corrosive agents, because whether it’s water or even chlorine from chlorinated fluids, the possibility for corrosion is always present.

“The inhibitor of choice is dependent on the metal being worked, the corrosive agent present or the type of fluid that is in use,” Cuneo continues. “Regardless of which parameter, the intent is to provide in-process corrosion protection for the piece and the tool.” The choice of the appropriate corrosion preventive is more complex because there are many more considerations.

WHAT INFLUENCES CORROSION?
A lot more than just the presence of water. In fact, in a properly designed system operating in an optimal environment,
constant exposure to water creates little to no corrosion. Factors that can influence and initiate corrosion include:

- The environment
- Design characteristics
- Material compatibility
- Movement
- Temperature
- Control.

**Quality Control Checklist: Don’t…**

- Substitute a material with a proven track record on the basis of cost savings without considering possible loss of corrosion control.
- Use data without checking that the environment and conditions in use relate to those under which the data was collected.
- Ignore good practice guidelines.
- Ignore the possibility that small changes in the environment or operating conditions could have a dramatic affect on corrosion control.
- Forget to allow for excursions outside of the bounds of normal operating conditions.
- Assume maintenance procedures that seem easy to carry out on paper can be carried out as easily in practice.
- Leave corrosion control until the last step in the design process and rely on remedial control measures.
- Ignore the environmental impact associated with control measures, coatings or maintenance procedures.
- Extend the times for cleaning processes or surface treatments beyond manufacturer recommendations, as this can create problems.
- Ignore the possibility that combined action such as stress and corrosion could significantly reduce lifetimes.
- Use rate data for uniform corrosion to estimate lifetimes for localized corrosion.
- Use calculation of corrosion rates as a basis for design, when a better design could eliminate the corrosion problem.


**The environment.** When a material is exposed to or operates in an outdoor environment, minor elements can have a significant bearing on corrosion. These elements include elevation, humidity, sun exposure, soil conditions, temperature and, of course, rainfall. The corrosion rate is also aggravated by immediate surface contaminants such as grease, oil and dust.

**Design characteristics.** An improperly designed piece of equipment has pockets that drain poorly and retain liquids. Another poor design is parts that are unnecessarily exposed to corrosion-promoting environments. Especially at risk for corrosion-creating design flaws are drains, joints, flanges and welds.

**Material compatibility.** Metals may be incompatible with other materials they contact, especially other metals. Fabrication may create differences in metallurgical structure or alloy composition, allowing such corrosive conditions as decaying welds. These can occur in unstable stainless steel when changes in the weld metal and base metal composition result in loss of galvanic protection.

Also, a fluid may deliberately include metal particles that inadvertently lead to corrosion. For example, dissolved copper in contact with aluminum can cause pitting. Extra corrosion-preventing measures may be necessary, even when a metal is in contact with non-metals like plastics, concrete and wood.

**Movement.** Movement of the corrosion promoter and the movement of parts can significantly affect the rate of corrosion. Impingement happens when liquids (droplets, mist, etc.) come in contact with a metal surface. Steep liquid velocity gradients, where vapor-filled voids form and collapse supersonically, create shock waves that cavitate the metal surface. Therefore, careful consideration is important in choosing metals for moving components such as pump impellers that are susceptible to erosion, impingement and cavitation.

**Temperature.** Higher temperatures tend to increase corrosion. If temperatures are too high, materials may oxidize and scale. On the other hand, because corrosion needs moisture, the drying properties of high temperatures may be beneficial.

**Control.** To be effective from both cost and labor perspectives, the most comprehensive corrosion control mea-

Unlike the protecting patina that forms on copper when it oxidizes, rust is purely destructive.
sures are appropriate where the consequences of failure are most serious, and those measures are capable of reducing risk to an acceptable level. Basic control categories include designing a corrosion allowance into the device, diligent surface cleaning and the application of coatings.

“Rust preventives should be used when the cost of applying the rust preventive is less than the cost of letting the metal rust,” Kingston says. “In some cases, there is little or no cost for just letting it rust. Manhole covers or sewer grates are permitted to rust with no consequence, so rust preventives are not used. Automotive parts and consumer goods are almost always protected by rust preventives at all stages to preserve their appearance and function.”

Within these categories, there are many corrosion-control measures available. Some are “corrosion inhibitors” and others are “corrosion preventives” (though experts disagree as to whether corrosion can truly be prevented).

CORROSION RATE
Once corrosion is present, the rate of corrosion becomes important. It is usually measured in one of two ways:

1. The ratio of weight loss between unit of area and unit of time
2. The rate of penetration, (the volume of metal lost).

In systems involving direct or indirect contact with water, factors affecting the rate of corrosion are:

1. **Water type.** This is more important than most people suspect. Hard (scale-forming) water tends to associate with low corrosion rates.
2. **Flow rate.** In general, the faster the water flow, the more corrosion. As water flow increases, there is increased corrosion-propagating oxygen at the surface, which tends to erode protective surface film.
3. **Environmental pH.** When the pH falls below 4, corrosion increases rapidly.

4. **Environmental oxygen content.** An increase in oxygen concentration for any reason usually increases corrosion.

INHIBITORS/PREVENTIVES: HOW THEY WORK
Rust is electrochemical in nature with the anode, cathode, electrolyte and conductor all present with a wet piece of metal.

“The temporary rust preventive interrupts one of these ‘battery’ components and thus stops the electrochemical process,” Kingston explains. “Typically, temporary rust preventives block the wet electrolyte from reaching the metal surface, thereby stopping the rusting process.”

As corrosion forms, bubbles and flakes off, fresh iron is exposed, and the corrosion process continues until all of the base material is either consumed or all of the oxygen, water, carbon dioxide and other corrosion-inducing agents in the system are removed or consumed. This is where corrosion inhibitors come in. The effectiveness, or corrosion-inhibition efficiency, of a corrosion inhibitor is a function of many factors, including but not limited to fluid composition, water quantity and flow.

There are several ways that corrosion inhibitors decrease the rate of corrosion, and there are several types of corrosion inhibitors, including cathodic, anodic, adsorption, mixed inhibitors, oxygen scavengers and microbicides. Each works best with a specific type of metal or alloy. The most successful corrosion inhibitors can reduce the corrosion rate of a metal or alloy by as much as 99%.

**Cathodic inhibitors.** Cathodic protection inhibits corrosion on submerged or buried formations by supplying an electrical charge that suppresses the electrochemical reaction that fosters corrosion. If correctly applied, corrosion can be stopped completely.

In its simplest form, this type of corrosion inhibition is achieved by attaching a sacrificial anode that converts the iron or steel into the cathode. The sacrificial anode is made from a substance with more negative electrode capacity than iron or steel such as zinc, aluminum or magnesium.

For example, zinc oxide interrupts the corrosion process that reduces water to hydrogen gas. As an alternative, oxygen or nitrate also can be reduced with a similar end result. One of the most common cathodic inhibition processes is steel galvanization.

**Steel galvanization.** Steel is galvanized by covering it with a zinc coating only a few thousandths of an inch thick. Zinc is used because it is more reactive than iron and consequently will sacrifice itself, leaving the iron untouched by corrosion. But because the zinc coating is sacrificing itself, galvanized coatings have a finite life if left unprotected. This life, measured in decades, is dependent on the thickness of the zinc coating. Additional corrosion-preventive coatings, such as paint, can dramatically increase the zinc coating’s lifespan.
Zinc is most often used because it's inexpensive, adheres well to steel and provides additional cathodic protection to the steel surface. This becomes important if the zinc layer is pierced (often at seams and joints). In more corrosive environments, like salt water, cadmium is preferred over zinc. More modern galvanization processes add aluminum, which migrates to cover scratches.

**Anodic Corrosion Inhibitors.** This corrosion inhibitor, commonly chromate, forms an anticorrosion layer on steel or aluminum surfaces. A significant downside is that this type of anodic corrosion inhibitor is a proven human carcinogen. In fact, the inclusion of chromate in some products is banned. For this reason, expert advice is crucial before considering the use of anodic inhibitors.

Another anodic corrosion inhibitor is pertechnetate, but like chromates, there is a major drawback. Its technetium family is a radioactive isotope—more radioactive than even uranium. Its use is restricted to tightly controlled areas such as nuclear reactors. Nitrites and phosphates can be more attractive alternatives. It's important to remember that if the concentration of anodic inhibitor is too low, it can actually aggravate pitting corrosion because it forms an irregular layer.

**Adsorption Corrosion Inhibitors.** Many organic inhibitors work by adsorption. The resultant film of chemisorbed inhibitor is then responsible for protection either by physically blocking the surface from the corrosion environment or by retarding the electrochemical processes. Adsorption inhibitors must have polar properties in order to be adsorbed (amines). Often, these molecules have two functions. They contain a hydrophilic group, which adsorbs onto the metal surface and an opposing hydrophobic group, which creates a limit.

**Paint.** Corrosion inhibitors are often added to paint, making paint an adsorption inhibitor. A pigment with anticorrosive properties is zinc phosphate. Compounds derived from tannic acid or zinc salts of organonitrogens can be used together with anticorrosive pigments.

“Temporary rust preventives can be usefully differentiated from more permanent protective coatings such as paints by their ease of removal,” Kingston explains. “Paints are not designed to be removed while temporary rust preventives are designed for removal whether they are removed in practice or not.”

**Mixed corrosion inhibitors.** Mixed corrosion inhibitors use processes from both anodic and cathodic corrosion inhibition to protect surfaces from corrosion. The best example of this process is steam. If used properly, steam passing through machinery, such as boilers and drive turbines, protects the pipes it passes through.

**Oxygen scavengers.** Hydrazine and a number of antioxidants, such as ascorbic acid, reduce the rate of corrosion in aqueous environments like boilers by eliminating the dissolved oxygen in the water. But because hydrazine is a very toxic carcinogen, its use is not often recommended. Another oxygen scavenger is sulfite.

**Microbicides.** High fluid bacteria counts are a primary cause of corrosion. The bacteria metabolize into mild organic acids that lower the pH of the fluid and create a friendly environment for corrosion. While the simplest solution is to drain the old fluid and clean the machinery, this isn't always practical. Oil field equipment is a good example. A viable alternative is to treat the fluid with a microbicide (antiseptic) to control and prevent future bacteria growth. Benzalkonium chloride (also used in a number of household products, including hand sanitizers) is commonly used in the oil industry.

**Others.** Covering steel with concrete provides protection to steel by creating a high pH environment at the steel-concrete interface. Chrome and tin plating involves the electrolytical application of a thin layer to the steel surface. This provides both corrosion protection and (in the case of chrome) an attractive, highly polished appearance. Because of this, chrome-plating is evident in the silver-colored components of things like bicycles and motor vehicles.

Bluing is a technique that provides limited resistance to corrosion for small steel items like firearms. The bluing is the electrochemical conversion coating that results from an oxidizing chemical reaction with iron that selectively forms magnetite (which is a black oxide of iron). This black oxide, however, provides little protection against corrosion unless the surface is also rubbed with oil to reduce moisture. Early gunsmiths used a similar chemical process that resulted in a brown finish called browning.

Corrosion inhibitors are tested according to the ASTM D665 Corrosioning Test. This test exposes a steel rod to a mix of oil and saltwater that has been heated to 140 F (60 C). If the rod shows no sign of corrosion after 24 hours, the fluid is considered satisfactory with respect to corrosion-inhibiting properties.
CHOOSING A PREVENTIVE

In addition to paints and glazes, corrosion preventives are commonly added to industrial fluids such as fuels, engine oils, coolants, hydraulic fluids and boiler water. Cuneo explains the six basic considerations for determining the correct corrosion preventive:

1. **Type of metal.** Whether it's aluminum, steel, galvanized, magnesium or composite, metal type dictates which additive is required.

2. **Cleaning agent.** Will the part be cleaned and, if so, with what—water, alkaline cleaner or another cleaning agent?

3. **Application method.** If the parts are wet and the corrosion preventive is applied by spraying, brushing or drip-coating, the product must be water-displacing to remove the cleaning agent from the metal surface. If the part is to be dip-coated, the product must not only be water-displacing but also water-separating (non-emulsifiable) to enable the water, removed from the metal, to separate from the fluid and fall to the tank bottom to be drained later.

4. **Storage and transportation parameters.** It is important to know what conditions will be encountered if storage is required. Indoor or outdoor? Short term or long? High humidity, salt atmosphere or acid fumes? Whichever it is, the more severe the environment, the more heavy duty the corrosion preventive must be. If the parts are to be stored in bins where there's going to be metal-to-metal contact, a non-staining additive is required. Transportation often requires more heavy-duty corrosion-preventing additives, especially when exposed to the elements such as on the back of an uncovered transport.

5. **Handling and exposure.** Pieces that are going to be handled after coating and during storage should have a corrosion preventive that deposits a dry-to-touch film. Films that provide longer-term protection are usually greasy in nature. This film type has a tendency to be thicker and self-healing and also provides protection during periods of covered transportation. Heavy waxy films are required for outdoor protection and are resistant to severe weather conditions, UV rays and salt atmospheres. Oily films will usually be the least protective, and coated parts are usually stored indoors for short to moderate periods of time.

6. **Dilutents.** The best protecting films are deposited out of solvent, and the least protecting are deposited out of oil. Emulsion-deposited films fall somewhere in between.

PREVENTIVES AS LUBRICANTS

Rust preventives can provide lubricity. Kingston says this usually comes from the oil carrier that forms the bulk of the rust-preventive formulation. “For example, a formulation that is 95% oil and 5% rust preventive additive will generally provide good lubricity,” he explains. “Replacing part of the oil component with solvent will decrease the oiliness of the protective film. If more lubricity is called for, additives in addition to rust preventives can be included. These can be antiwear or extreme-pressure additives of the type commonly used in MWFs or circulating lubricants.”

The additives Kingston refers to tend to also be surface active. In some cases, they compete with the polar rust preventive additives and seriously degrade the rust preventive performance. This means the formula needs to be balanced so it provides both lubricity and rust prevention.

“Rust preventives are often multifunctional formulations with rust prevention being the major focus or only one of many performance characteristics,” Kingston says. “In addition to rust prevention, other common performance requirements include lubricity, penetration, resistance to staining, surface finish appearance as well as corrosion control for non-ferrous metals.”

To prevent corrosion, hydraulic fluids include corrosion inhibitors that deposit a protective film on metal surfaces. The film is impervious to water and, once the film is established throughout the hydraulic system, completely prevents corrosion. In order to prevent fluid breakdown and the acid formation that causes corrosion, these additives must exhibit excellent hydrolytic stability in the presence of water.

In addition to hydraulic fluids, corrosion inhibitors are commonly added to fluids such as coolants, fuels, engine oil and boiler water.

“Corrosion inhibitors are in the formula for corrosion protection but seem to have a minimal impact on lubricity,” Cuneo says. “Some, especially amine borate types, will augment the lubricity of a fluid, but the intent is corrosion protection and most fluids contain much stronger lubricating packages.”

TRENDS

In the last several years, there has been movement toward water-soluble or water-emulsifiable products. The attempt to develop a water-based product that deposits a dry film—and dry in a reasonably short time—has had limited success, though. Problems with emulsion stability, re-emulsification in high humidity conditions and short-term corrosion protection continue.

“With the trend of machining lighter metals, like aluminum and magnesium, corrosion inhibitors for these types of metals are being sought,” explains STLE-member Jack Kimes, Midwest business manager for Focus Chemical in
North Olmsted, Ohio. “Also, regulatory legislation throughout the world is causing MWF formulators to look for boric acid alternatives and develop amine-free fluids. Therefore, development efforts for new corrosion inhibitors include boric acid and/or amine-free additives designed for aluminum/magnesium machining.”

Some of these types of products are already beginning to enter the market, and Kimes expects more soon.

Experts like Cuneo say that the reduction of allowable VOCs will have a significant impact on corrosion preventive performance. This is because reducing the amount of volatile solvents in the finished corrosion-preventing fluids alters the deposited film type, which, in turn, reduces the length of time the metal is protected from corrosion. Also, deposited films have reduced additive content due to lower volatility solvents evaporating at a slower rate or not evaporating at all. The result is that corrosion-inhibiting products may need reaplication.

As far as corrosion inhibitors are concerned, VOC content should have minimal effect because corrosion inhibitors are generally water- or oil-based.

“I believe another issue that will become more and more important is the use of renewable resource raw materials,” Cuneo says.

He has been developing renewable resource corrosion preventive additives and finished fluids that produce equivalent performance at a cost that is competitive with traditional petroleum-based products.

Renewable resource solvents do have their drawbacks, including lack of evaporation and high cost. Cuneo expects the cost to go down as manufacturing procedures increase yields and quality. He also thinks technology will eventually address the slow- to no-evaporation problem.

Kingston agrees. “Changes in rust preventives are being driven by two major forces. The first is government regulations designed to achieve health, safety and environmental goals. The second is more demands from end-users to improve function and lower costs.

“End-users need to comply with these worldwide governmental regulations, and they need to do this while also reducing costs and increasing performance to meet worldwide competition. Rust preventive additives and formulations are continually changing in an effort to meet these two, often contradictory, driving forces.”

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